PB84-119940

Intercomparison of Periodic Fine Particle Sulfur and Sulfate Concentration Results

(U.S.) Environmental Sciences Research Lab.
Research Triangle Park, NC

Nov 83

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1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-83-105		PB84 119940

4. TITLE AND SUBTITLE	5. REPORT DATE
INTERCOMPARISON OF PERIODIC FINE PARTICLE SULFUR AND SULFATE CONCENTRATION RESULTS	November 1983
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) David C. Camp, R. J. Paur and R. K. Stevens	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Sciences Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711	10. PROGRAM ELEMENT NO. CDTA1D-01-023 (FY-82) 11. CONTRACT/GRANT NO. D0947NASX
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 277]]	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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Normalized results at all sulfur concentration levels measured for five of the six samplers were 1.0 ± 0.05. The sixth set gave a result of 0.60 ± 0.14. After revised results were resubmitted for the sixth set, normalized results for the six sets of hourly sulfur results agreed to within ± 8% of their composite-mean values, with standard deviations varying from 9 to 22%. One participating group operated three similar samplers, each calibrated by a different method, that gave normalized results of 1.06 ± 0.12, 0.93 ± 0.22, and 1.54 ± 0.25.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	61
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB84-119940

EPA-600/3-83-105
November 1983

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RESEARCH TRIANGLE PARK, NC 27711

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SPRINGFIELD, VA 22161

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ABSTRACT

A one-week study was conducted in August 1979 to evaluate the comparative ability of representative aerosol sampling systems to monitor fine particulate sulfur and sulfate concentrations periodically in situ. Participants in the study operated their samplers simultaneously in the same location for the duration of the study. Samplers tested included five modified flame photometric detection instruments and two dichotomous samplers, including one sampler designed to yield near-real-time sulfur concentrations from on-line, wavelength dispersive X-ray fluorescence analysis of the fine particle filter substrate. All but one of the samplers were operated from a common duct located within the same laboratory; the other was operated on the roof of the building.

Concentration results intercompared consisted of six sets of hourly fine particulate sulfur values, three sets of 6-h sulfate values, and three sets of hourly sulfur results based on different calibration methods from the same participant. Some periodic mass measurements were also obtained, but were not compared.

Daily midafternoon sulfur excursions were observed with numerous less-than-one-hour minimum to maximum concentration changes within the excursions. Air stagnation during the last 40 h of the study drove the sulfur and sulfate concentrations to almost 9 and 21 $\mu g/m^3$, respectively. Throughout the study the sulfate to sulfur concentration ratio remained at 2.22 ± 0.14, a value 26% less than expected. This suggests that either all of the sulfur did not occur in sulfate form or the sulfate could not be completely extracted from the filter media. Mean 6-h sulfate and mass concentrations gave an observed correlation of $\overline{SO_4} = 0.5(M_f - 18)$ with a correlation coefficient of 0.91.

Normalized results at all sulfur concentration levels measured for five of the six samplers were 1.0 ± 0.05. The sixth set gave a result of 0.60 ± 0.14. After revised results were resubmitted for the sixth set, normalized results for the six sets of hourly sulfur results agreed to within ± 8% of their composite-mean values, with standard deviations varying from 9 to 22%. One participating group operated three similar samplers, each calibrated by a different method, that gave normalized results of 1.06 ± 0.12, 0.93 ± 0.22, and 1.54 ± 0.25.

Results from all of the sampler measurements made during this study indicate that individually reported sulfur concentration measurements may be in error by a factor of up to 2, higher or lower, due to miscalibration of the sampler. Only the development of better sulfur and sulfate standards and periodic intercomparison participation can minimize the likelihood of such errors.

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ACKNOWLEDGMENTS

The authors are grateful to the participants from each laboratory and university who made the intercomparison study possible. Encouragement provided by Dr. A. P. Altshuller, Director of EPA-ESRL, and by Dr. W. E. Wilson of EPA-ESRL during the formative stages of this study was essential and is also greatly appreciated. In addition, the authors thank Geoffrey Cobourn and Rudy Husar of Washington University, St. Louis, for their assistance in an earlier draft of this report for journal publication.

SECTION 1

INTRODUCTION

Sulfur-containing compounds emitted into the ambient air, primarily from the burning of fossil fuels, have long been known to degrade atmospheric visibility. These compounds may additionally be harmful to human health. Sulfur (S) can occur in various chemical states, that is, as sulfur dioxide (SO_2) gas, in acidic form such as sulfuric acid (H_2SO_4), or in the form of metal sulfate salts. In an earlier intercomparison study (1,2), sulfur and sulfate ($SO_4^=$) were among 12 environmental pollutants monitored for sixteen 12-h periods over 8 days by several different types of aerosol samplers. Results from that study indicated that 88% of sulfur was concentrated in the fine mass fraction ($\leq$ 3 particle diameters), while $SO_4^=$ showed a 94% concentration in this fraction.

Many sampling techniques (3) have been developed for monitoring ambient concentration levels of sulfur and its various compounds, and many procedures have been defined for the chemical analysis of the samples collected (4,5). Because sulfur-containing aerosol particulates have such a significant effect on the environment, and because interest in both source-receptor and concentration-effect relationships is growing, rapid and accurate monitoring of ambient sulfur concentrations is becoming increasingly important. Recently, several new *in situ* techniques have been developed (6-10) that use flame

photometric detection (FPD) methods to measure particulate sulfur concentrations. Each instrument employs different modifications to the Meloy Model SA-260 or SA-285 sulfur analyzers to perform the in situ analysis. The FPD technique is capable of monitoring ambient sulfur concentrations with a time resolution on the order of one minute.

Energy dispersive X-ray fluorescence analysis has also demonstrated an ability to perform multielement analysis of ambient aerosol filters, particularly in tandem with impactor-type samplers (3). A small, transportable aerosol sulfur monitoring instrument employing wavelength dispersive X-ray fluorescence analysis has been developed (11), which collects fine particulates directly on filter substrates and performs a sulfur analysis with a typical time resolution of 30 min or less.

The proliferation of FPD-based instruments and the development of the new X-ray based technique naturally raise the question of how comparable their respective results are. Differences in the ways these various intruments perform sulfur measurements and in the procedures used for their calibration can lead to disparate measured concentration levels. Thus, it is important to determine how large these differences can be, and if possible, to illuminate the faults in measurement and calibration procedures that can lead to biased results.

An in situ sulfur monitoring study was designed so that hourly sulfur concentration results and 6-h $SO_4^{=}$ and mass concentration results from several

types of samplers could be intercompared. Participants were invited to bring their instruments to a Washington University (WU) campus laboratory and to operate their sampling systems simultaneously with others throughout the study. The procedures followed were similar to those used during an earlier study carried out in Charleston, WV (1,2).

Since the types of instruments used in the WU (St. Louis, MO) field study are similar to those used in both state and federally funded environmental programs to monitor sulfur, results from this study are indicative of the quality and intercomparability of concentrations obtained throughout the country. They are also indicative of the care necessary in calibrating instruments and the importance of the calibration techniques employed in determining results.

SECTION 2

CONCLUSIONS

At relatively high sulfur concentrations ($\geq$ 6 $\mu g/m^3$), all six sampling systems reported hourly results that agreed to within ± 25% of their combined hourly composite-mean concentrations. For five of the six samplers measuring sulfur, the average ratios of all hourly concentrations reported to their hourly composite-mean values were within ± 5% of 1.0. Standard deviations for four of the five result sets were less than 10%, while the fifth set gave 21%. The sixth sampler suffered a calibration error that gave predominantly lower concentration results.

At relatively high $SO_4^=$ concentrations ($\geq$ 14 $\mu g/m^3$), all three samplers reporting $SO_4^=$ results agreed to within ± 10% of their composite 6-h means.

All samplers were able to track the relatively sharp sulfur concentration peaks or excursions that occurred daily. Maximum concentrations in these transient (1- to 4-h) spikes reached four to six times the background concentrations ($\sim$ 1.5 $\mu g/m^3$). The source and nature of these short, multipeaked excursions were not sought.

The highest sulfur concentrations measured in St. Louis during air stagnation (~ 9 $\mu g/m^3$) were equivalent to those recorded during a similar air stagnation period that occurred in the Charleston, WV, intercomparison study held in 1976 (1,2), but minimum concentrations observed in St. Louis were half those observed in Charleston.

Regression analysis of 6-h composite-mean $SO_4^=$ concentrations versus equivalent 6-h averages of the hourly sulfur composite-mean concentrations gave a $SO_4^=$ to sulfur ratio of 2.2 for the St. Louis study, versus 3.0 observed in the Charleston (1,2) and Philadelphia (3) studies. This lower ratio was independent of concentration level; i.e., it remained the same for relatively clean air (background sulfur levels), for transient sulfur excursions, and for stagnant air. Thus, either all of the sulfur did not occur in $SO_4^=$ form, or the $SO_4^=$ could not be extracted completely from the filter (by three independent groups).

Use of a common duct to route air to a distribution of samplers proved satisfactory. Two samplers connected to this duct that measured $SO_4^=$ gave very similar results to a third sampler located on the roof.

Out of a total of 11 sampling systems measuring either sulfur or $SO_4^=$, five suffered slight to substantial calibration errors. Brookhaven National Laboratory (BNL) resubmitted results based on a revised calibration. Regression results gave a slope of 0.88 ± 0.02 for the original results versus 1.20 ± 0.03 for the revised results, with no change in their intercept of -0.65 $\mu g/m^3$.

The host institution, Washington University, operated three similar sampling systems that used separate methods of calibration. Their results, based on an ammonium sulfate $(NH_4)_2SO_4$ calibration, were best (1.06 ± 0.12, an average of all hourly concentration results relative to the composite-mean values). Results based on particulate sulfur calibration were good (0.93 ± 0.22, and results based on an SO_2 calibration method were poor (1.54 ± 0.25). The latter sometimes gave concentration results over a factor of 2 high.

If either the WU results based on the SO_2 calibration or the original BNL results had been the only set of measurements made at St. Louis, reported hourly sulfur concentrations would sometimes have been as much as a factor of 2 higher or lower than the consensus composite-mean values. These large discrepancies emphasize the importance of accurate, careful, and thorough calibration of all sampling systems, and the need for intercomparison studies to insure consistent results.

Although fine mass (M_f) concentrations were recorded only as a matter of interest, an unexpected fine mass versus $SO_4^=$ correlation was observed. Furthermore, analysis of similar data obtained during the earlier Charleston intercomparison study (1,2) revealed the same correlation. That is, half of the fine mass collected above a threshold of 18 $\mu g/m^3$ appears to come from $SO_4^=$-related species, $(M_f - 18)\ \mu g/m^3 = 2(SO_4^=)\ \mu g/m^3$. An examination of this mass-$SO_4^=$ relationship in other parts of the country would prove interesting.

SECTION 3

RECOMMENDATIONS

This intercomparison study has demonstrated that the feedback individual investigators receive from such studies on sampling system performance and concentration results is extremely valuable. Therefore, it is recommended that all publicly funded monitoring programs within logical groupings participate in initital and subsequent periodic side-by-side intercomparison studies to insure that pollutant concentration results are consistent.

U.S. Environmental Protection Agency (EPA) contractors should also be strongly encouraged to participate in intercomparison studies in order to reveal any variations in their reported pollutant concentrations. Any differences resulting from measurement and/or calibration biases should be resolved before the instruments are deployed for field measurements.

Widely divergent sulfur concentrations reported by one participant from three similar sampling systems, which differed only in the calibration method used, suggest the need for the development of ASTM-type aerosol calibration standards for sulfur and $SO_4^=$. Without such standards, there will be doubt as to the relative accuracy of sulfur and $SO_4^=$ concentration values reported in the literature, but obtained by different instruments at different times in different regions of the country and by different investigators.

SECTION 4

EXPERIMENTAL

SAMPLING SYSTEMS

All measurements were made continuously for 1 week from August 3 to 10, 1979, at Washington University, St. Louis, Missouri. The instruments were assembled in a fourth-floor laboratory at the Center for Air Pollution Impact and Trend Analysis (CAPITA). The WU campus is located in a suburb 10 km west of downtown St. Louis. Each sampler system was connected to a common duct as shown in Figure 1, except for a sequential hi-vol sampler operated by BNL on the roof (5th floor). This sampler was used to obtain 6-h $SO_4^=$ concentrations. The sampler's location on the roof allowed collection of ambient air concentrations with which concentrations obtained from air taken in through the duct one floor below could be compared. Figure 1 notes that some participants brought more than one sampler to the study site. Table 1 lists relevant information concerning the type of sampling system(s) operated by each participant and summarizes the frequency of pollutant concentrations they reported.

The five FPD instruments used in the study each employed different modifications to adapt the flame photometric methodology to in situ measurement of particulate sulfur. Four of the five systems employed a diffusion tube denuder to remove SO_2. The WU system used a temperature programmed heater to

perform *in situ* thermal analysis of the $SO_4^=$ aerosol (6), thus providing information on the chemical compounds present. The Oregon Graduate Center (OGC) system also performed *in situ* thermal analysis using three tubes at different temperatures and a fourth tube with an absolute aerosol filter for setting the instrument zero (7). The Environmental Research and Technology, Inc. (ERT) system had a modified burner block inlet; zeroing was done manually with an aerosol filter (10). The BNL system used denuder temperature cycling for H_2SO_4 speciation, a sulfur hexafluoride (SF_6)-doped hydrogen supply for signal enhancement, and automatic zeroing by filter (9). The National Bureau of Standards (NBS) system used a pulsed electrostatic precipitator to remove particles alternately. This system did not use a denuder. Rather, ethyl mercaptan addition was used to enhance the signal so that both total sulfur and gaseous sulfur were measured directly, and particulate sulfur was obtained by difference (8). Two of the systems (WU's and ERT's) used the standard Meloy 285 electronics for signal processing. Two other systems (OGC and BNL) measured current directly with high resolution electrometers. The NBS system used a lock-in amplifier to process its modulated signal. The transportable wavelength X-ray fluorescence analysis system performed an analysis on the filter from the fine particle section of an automated dichotomous sampler (11).

A Beckman automated dichotomous sampler collected fine particle aerosol every 6 h on Teflon filters. Sulfate was extracted and analyzed by ion chromatography according to procedures described earlier (3). The BNL sequential hi-vol sampler was operated on the roof independently of the other samplers.

The ERT sequential sampler (10) was operated to obtain $SO_4^=$ concentrations but was located at the end of the common duct.

Some fine particle mass concentrations were reported, but these measurements were not the focal point of the study. Nevertheless, the fine particle mass concentrations obtained in St. Louis can be compared with those obtained in other field studies. Integrated 6-h mass concentrations were obtained from the EPA dichotomous sampler. One of WU's TWOMASS samplers reported hourly mass values regularly, but only for the last half of the study. Their other TWOMASS sampler reported hourly concentrations, but at irregular hours and only for three or four of the hours within a 6-h period.

Finally, WU was able to obtain three sets of sulfur concentrations based on three different calibration methods. The first used flash vaporization coupled with FPD of particulate sulfur. The second was an in situ FPD method that used SO_2 for calibration, and the third was also an in situ FPD method, but concentration results were based upon an $(NH_2)_2SO_4$ calibration.

CALCULATION OF COMPOSITE-MEAN CONCENTRATIONS

When the actual ambient pollutant concentrations are unknown, a reference concentration can be established by averaging all mean concentrations for each pollutant specie measured, provided certain minimum conditions are met. These conditions are that only one result set per participant be allowed, that all periodic results be examined for outlying values, and that no sulfur or $SO_4^=$ result sets be accepted that reported less than 50% of all possible observations.

Generally, in a field study of this kind, no sampler is regarded as giving the "correct" concentration; therefore, if all concentration results are accorded equal weight, then a composite-mean concentration can be calculated for each measurement period for each pollutant. For hourly or 6-h results, the composite mean is defined simply as the mean value of all valid concentration results reported for each hourly or 6-h period. Regression analyses can be performed for each sampler versus the composite mean, or if desired, relative to any other sampler of choice. Regression analysis results for all samplers and pollutants are discussed in the RESULTS section.

OUTLIERS

Although some participants at the study operated more than one sampler, only one result set per participant was accepted for the purposes of intercomparison of sulfur concentrations, or for the calculation of a composite mean. Because of the irregularity of the mass concentrations reported, all values submitted were used. After calculating composite-mean values for sulfur and $SO_4^=$, all contributions to each mean value were examined for outliers. The Dixon criterion (12) was used with α set equal to 10%. Any values falling outside 90% of all values reported for a given observation period (lowest, highest 5% $\equiv 1/2\alpha$) relative to the composite mean were considered for rejection. No outliers were found in either the 6-h $SO_4^=$ or 6-h mass concentration results. Among the hourly sulfur values, only 4 outliers in 918 values submitted were found, all from the ERT sampler. For these four periods, composite-mean values were recalculated with the four outlying values removed.

The mean concentration for any hourly or 6-h period was calculated from the expression

$$M = \frac{1}{n} \sum_{i=1}^{n} C_{ij}, \qquad (1)$$

where C_{ij} is the concentration reported by the i-th sampler for the j-th period, and n is the number of sampler sets contributing to M_j.

SECTION 5

RESULTS

Eight sets of hourly sulfur concentrations, three sets of 6-h $SO_4^=$ concentrations, and three sets of fine mass concentrations were submitted. From the eight sets of hourly sulfur concentrations reported, six were from independent participants, and each provided a sufficient number of result sets to carry out a meaningful comparison. The three sets of hourly sulfur concentrations submitted from WU provided an interesting intercomparison in and among themselves. Although one of the three sampler systems reporting $SO_4^=$ concentrations was operated on the roof, all three result sets were in good agreement with each other. The three sets of fine particle mass concentration results were reported from such different bases that no intercomparison was possible. Instead, only the 6-h composite-mean mass values were used to examine possible correlations that might arise between $SO_4^=$ and mass. Each pollutant is discussed in more detail in separate sections that follow.

HOURLY SULFUR CONCENTRATION MEASUREMENTS

Six of the seven participants reported a sufficient number of hourly sulfur concentrations so that their results could be compared. Individual results are listed in the Appendix. The study began at 1900 central daylight time (CDT) August 3, 1979, and continued through 1800 CDT, August 10, 1979.

Five of the possible 168 hours were devoted to a calibration experiment, leaving 163 one-hour periods for intercomparison of measurement results. Most participants experienced occasional trouble with or malfunction of their samplers, which prevented them from reporting data for all 163 periods. The number of missing results varied from 4 for 2 participants (BNL and LBL) to 23 for NBS. The average was 12 missing periods per investigator. Table 1 summarizes the number of missing periods for each participant. Fortunately, each participant's missing values occurred randomly throughout the duration of the study, thus allowing 163 hourly composite-mean sulfur concentrations to be calculated.

Figure 2 shows a plot of the 163 composite-mean sulfur concentrations in $\mu g/m^3$ versus time (hourly) for the duration of the study period. The shaded 5-h band (2300 CDT, 8/8/79 to 0400 CDT, 8/9/79) indicates the calibration period. Two features of this week long study of sulfur concentrations stand out as significant--the transient concentration spikes and the high sulfur levels that persisted for a day and a half. The high concentration levels were apparently due to air stagnation that occurred at the end of the study period. The sulfur concentrations observed during this episode were nearly as high as those observed in stagnant air at Charleston, WV (1,2). However, in Charleston, air stagnation only doubled the average background sulfur concentration ($\sim$ 3 $\mu g/m^3$). In St. Louis it exceeded four times the average background concentration ($\sim$ 1.5 $\mu g/m^3$).

The transient spikes appear to be a different phenomenon. Prior to air stagnation, these events occurred daily within about two hours of 1600 CDT. They usually lasted several hours but were as short as one hour (8/6/79) or as long as six hours (8/4 and 8/7/79) in duration. The highest peak concentration reached almost 10 $\mu g/m^3$. Furthermore, they contained more structure than is apparent from the 1-h time scale observations offered in Figure 2. An example of the fine structure within one of these transient spikes (8/8/79) is shown in Figure 3. These data were recorded by one of the BNL samplers that made three sulfur concentration determinations per minute. These transient spikes appear to be a single cloud of higher than average sulfur concentrations, within which there exist distinct plumes of varying concentration. Within 1 h, the concentration moves from one maximum value through a minimum and back to a second maximum value. Although the single peak observed near 1800 CDT on August 8 in Figure 2 is broadened towards later time, the integrated hourly results cannot show the fine structure of three distinct peaks seen in Figure 3. The small peak observed just past 2000 CDT in Figure 3 is sufficiently separated in time to show up as a satellite peak in the hourly observations of Figure 2. None of the six sets of hourly concentrations reported could give any indication of substructure in these spikes, although the raw data might have if their field measurements had had better than 15-min time resolution. Clearly, instruments reporting concentration levels integrated hourly would not be capable of observing such fine structure.

The hourly concentrations reported by each participant are shown in Figure 4; however, the composite-mean hourly concentration values (Figure 2) are not included. Because of the small scale of Figure 4, any given sampler's

results may be difficult to follow throughout the study; nevertheless, each institution's results are identified at several places within the figure. Every sampler did record the transient sulfur spikes as well as the persistent higher concentrations present during air stagnation. The BNL sampler frequently reported relatively lower concentrations, and the ERT sampler often reported higher values.

The relative deviations from the hourly composite-mean values for each sampler reporting sulfur concentrations are shown more clearly in Figure 5. Here each sampler's hourly results have been divided by the corresponding hourly composite-mean concentration values. Note that the BNL sampler appears to suffer from a calibration error that affects low concentration values more seriously than high concentrations. Low ambient sulfur levels of about 1.5 $\mu g/m^3$ were reported by the BNL sampler to be only about 0.85 $\mu g/m^3$. Thus, the error for this sampler's results at low concentration is nearly a factor of 2, but decreases to only about 25% low at the highest ambient concentrations measured. Meanwhile, the ERT sampler reported stagnant air sulfur concentrations to be about 25% higher than the composite-mean values. This suggests a calibration error that becomes important only at higher concentrations for the ERT sampling system.

Once the intercomparison results were made known to the BNL group, they reexamined their calibration data. Upon receipt of BNL's recalibrated results (Tanner, R. L., private correspondence), revised hourly composite-mean sulfur concentrations were calculated for all six samplers in the original set, and each partipant's results were renormalized to the revised composite-mean

values. These renormalized results are shown in Figure 6. Comparison of Figures 5 and 6 shows the considerable improvement in the BNL results, particularly at the lower concentrations. Note that the revised and higher hourly BNL concentrations also cause a 7% increase in the composite-mean concentrations. In Figure 5 the composite-mean values for the period 8/9 to 8/10/79 occur below the WU data (dots), whereas in Figure 6 for this same period, the composite-mean values pass through the WU data. Also evident from Figure 6 is that the ERT sampler results show the largest variations in concentration results measured during the study.

Three sets of hourly sulfur concentrations were reported by WU and are shown in Figure 7 normalized to the original composite-mean values. Each data set was based on a different method of calibration to obtain the sulfur concentrations. Results based on an SO_2 calibration method were high and occasionally were a factor of 2 higher than the composite mean. The WU results based on particulate sulfur calibration were somewhat lower and showed considerably larger fluctuations than their result set based on $(NH_4)_2SO_4$ calibration (dots). Clearly, had their SO_2-calibrated results been the only set of results obtained and reported, the composite-mean values for the field study would have been considerably higher, and the bias in the WU data would have been evident.

More importantly, the SO_2-calibrated data set graphically demonstrates the necessity for careful calibration procedures and the importance of intercomparing one's own sampler performance with others of similar or different

operational principles. If during the period of this study the sulfur concentrations had been measured only by the WU group using the SO_2-calibrated FPD method, their reported results would have indicated pollutant concentrations 54% higher than the probable values and sometimes almost twice what they probably were. On the other hand, had the sulfur concentrations during this study been measured only by the BNL group using their unrevised calibration data, the reported sulfur concentrations would have been nearly half the probable values (composite means). Thus, results from this study suggest that sulfur concentrations reported in the literature from a single measurement instrument could be in error by as much as a factor of 2, either higher or lower than the actual ambient concentration levels present.

Individual investigators should be encouraged by the results from this study to seek every opportunity to compare their own sampling system results with results from others. Differences obtained in measured ambient concentrations would motivate resolution of the differences, especially if serious. Such differences might be caused by simple calibration errors. Results from this study also suggest that all state and federally funded monitoring programs should carry out periodic intercomparison studies of all instruments used to monitor selected environmental pollutants.

SIX-HOUR $SO_4^=$ AND MASS CONCENTRATION MEASUREMENTS

Table 1 indicates that three groups submitted results for $SO_4^=$ concentration measurements reported on the basis of 6-h periods. The 6-h results for these three groups are listed in Table 2. Although the BNL hi-vol sampler

was operated on the roof (not off the common inlet duct in the fourth-floor lab as were the other two $SO_4^=$ samplers), its reported concentration values agreed well with EPA's results and with both samplers at the higher $SO_4^=$ concentrations. Hence, 6-h composite-mean $SO_4^=$ concentrations were calculated assuming equal weights for each sampler's results. The magnitude of these 6-h mean values is shown by the dotted line in Figure 8 (left ordinate scale). Less structure is evident here than with the hourly sulfur results shown in Figure 2. Nevertheless, the widest transient sulfur spikes observed on August 4 and 7 and the narrowest spike observed on August 6 are correlated with the intensity of the $SO_4^=$ concentrations observed on those dates. The correlation with stagnant air is also good.

Too few $SO_4^=$ result sets were obtained in this study to warrant plots similar to those shown in either Figure 4 or Figure 5. As was the case for sulfur, the agreement obtained for $SO_4^=$ concentrations among the three samplers was best at high concentrations (often less than 10% total spread), and the greatest differences occurred at low concentrations. The ERT values were almost always less than the BNL values, which were usually in excellent agreement with EPA results.

Table 2 lists the 6-h results for the three labs reporting $SO_4^=$ concentrations and the corresponding 6-h composite-mean values. The column labeled CM S represents the 6-h average values calculated from the hourly composite-mean sulfur concentrations. The correlation between sulfur and $SO_4^=$ composite means is discussed in the following section.

Composite-mean 6-h mass concentration results have also been plotted in Figure 8 (right-hand ordinate scale). Table 1 indicates that three groups reported results for fine ($\leq$ 2.5 μm particle diameters) particulate mass. Again, mass concentrations were not the primary focus of this intercomparison study. They were obtained partly as a test of several new samplers (WU) and partly to obtain information on the fine particulate mass concentrations encountered during the study. The EPA sampler reported 6-h integrated mass concentration values. One of WU's TWOMASS samplers reported hourly mass values regularly, but only for the last half of the study, and their second sampler reported hourly concentrations, but at irregular hours and only for three or four of the hourly periods within each 6-h interval. Thus, the only way to make use of the reported data was to calculate 6-h mean mass concentrations for the two samplers reporting hourly results, then calculate 6-h composite-mean concentrations for the three result sets. The same 6-h intervals used in calculating the $SO_4^=$ means were used to calculate the mass results. The time variation in the composite-mean mass concentrations are shown by the dashed line in Figure 8. Note the suppressed zero for the mass scale (right ordinate). Comparison of these results suggests a correlation between 6-h ambient $SO_4^=$ concentrations and fine particulate ($\leq$ 2.5 μm) mass concentrations. The correlation is discussed below.

REGRESSION ANALYSES

Regression analyses were performed between appropriate composite means and all of the sulfur, $SO_4^=$, and mass result sets submitted, as well as for

correlations between $SO_4^=$ versus sulfur and fine mass versus $SO_4^=$. As discussed above, there were six sets of hourly sulfur results which could be compared with two composite means, one using the original BNL data, and one using their revised data. Table 3 summarizes the regression analysis for all 163 hourly periods. The top portion of Table 3 shows the results of each lab (original BNL data) versus the composite means. The lower portion of Table 3 shows the correlation results obtained using a composite mean calculated with the revised BNL data. In the latter data set the ERT slope is nearer unity, but BNL's deviation from unity is larger for their revised data than for their original data. Neither the ERT nor the BNL intercepts changed significantly. The errors on the intercept and slope values shown in both sections of Table 3 correspond to a 90% confidence level, where R is the correlation coefficient and E is the standard error of the estimate in $\mu g/m^3$. It is apparent from Figure 5 that BNL's original data would yield a slope less than 1.0 relative to the composite mean, and the slope for ERT's data would be greater than 1. The slopes for the other four sets of hourly results do not differ significantly from each other. The calibration error of the original BNL results is reflected in its negative intercept, which causes the other four sampler intercepts to be positive. That BNL's revised results intercept is unchanged suggests that they simply increased all hourly results by a scale factor rather than a nonlinear correction factor indicated by regression analysis of their original and revised results.

Only three result sets were submitted for 6-h $SO_4^=$ concentrations. Table 4 summarizes the regression analysis for the 6-h $SO_4^=$ results versus

their composite-mean concentration values. The slopes of the EPA and BNL results differ by only a few percent, and both of their intercepts are consistent with zero to well within a 90% confidence limit. The ERT sampler used to obtain $SO_4^=$ concentrations appears to have a slight calibration error that leads to lower than average $SO_4^=$ concentrations, while the ERT sampler used to obtain sulfur concentrations gave somewhat higher than average sulfur concentrations. In general, agreement between the three $SO_4^=$ result sets was good.

A regression analysis was performed for the 28 six-hour composite-mean $SO_4^=$ concentration values versus the 28 six-hour average values for sulfur (with and without revised BNL results). Each average value was calculated using the appropriate six 1-h composite-mean values. The result gave $SO_4^= = (2.22 \pm 0.14)S$ with an intercept of 0.0 ± 0.56 $\mu g/m^3$ for the original BNL data compared to $SO_4^= = (2.13 \pm 0.14)S$ with an intercept of -0.07 ± 0.58 $\mu g/m^3$ for the revised BNL data. The errors on the slope values of the $SO_4^=$ versus sulfur correlation were small (less than 7%), and neither intercept indicated any bias. The correlation coefficients (0.98) for both were excellent.

The same correlation was examined separately for low (background) and high sulfur-$SO_4^=$ values. No difference was found (2.16 ± 0.44 for 13 low $SO_4^=$ values; 2.28 ± 0.33 for 15 high $SO_4^=$-sulfur values) using composite-mean values based on the original BNL results. This $SO_4^=$ to sulfur ratio does not agree with the value of 3.0 observed in the Philadelphia (3) and Charleston inter-comparison studies (1,2). Apparently, about 26% of the sulfur did not exist

in the form of $SO_4^=$ or was not extractable from the filters in the St. Louis study. Note, however, that all three groups reporting $SO_4^=$ must have had the same difficulty extracting the sulfur. Figure 9 shows a regression analysis plot of the 6-h composite-mean $SO_4^=$ concentrations versus the 6-h sulfur concentration mean values (original BNL results).

The lower section of Table 4 lists regression analysis results for 6-h fine mass concentration measurements. Correlation between the results was only fair. The three mass concentration result sets were reported from such different measurement bases that no intercomparison would be meaningful. The WU TWOMASS Sampler 2, which reported sporadic hourly concentrations, may have contributed a slight bias to the composite mean because it did not report values for every hour.

Figure 8 suggests evidence for a correlation between 6-h $SO_4^=$ composite-mean concentrations and fine particulate mass. A regression analysis of the 6-h fine mass means versus the 6-h $SO_4^=$ means gave $(M_f - 18) = (2.00 \pm 0.31)SO_4^=$ with an intercept of -0.29 ± 2.75 and a correlation coefficient of 0.91. This correlation is unexpectedly good, and, of course, the intercept is not expected to be zero; it is actually 18 $\mu g/m^3$, because of mass contributions from non-sulfur-related species such as the crustal elements.

Figure 10 shows a regression plot of the composite-mean $SO_4^=$-mass correlation data. Because the mass data were not the focal point of this study, this same correlation was examined for results obtained in the Charleston

study (1,2). Assuming the same intercept of 18 μg/m^3, the correlation gave $(M_f - 18) = (2.04 \pm 0.38)SO_4^{=}$. Since the Charleston data were quite extensive, obtaining similar results for the correlation between fine mass and $SO_4^{=}$ in both the Charleston and St. Louis studies was surprising. Results from both studies suggest a threshold concentration for fine mass independent of sulfur-related species. Above the 18-μg/m^3 threshold, half of any additional fine mass appears to be due to $SO_4^{=}$-related compounds. It would be interesting to examine this relationship in other regions of the country. The correlation found in these two field studies may be valid only for the central United States. That is, the threshold and/or correlation may not exist for the extreme northeast, the Florida peninsula, or the west coasts of Washington, Oregon, and California when on-shore winds control environmental pollutant levels.

SECTION 6

DISCUSSION

This side-by-side intercomparison study of sampling systems was designed to measure ambient concentrations of sulfur and $SO_4^=$ in August of 1979 in St. Louis. The study successfully demonstrated for the sampling systems brought to the study that concentrations of these two sulfur-related pollutants can be determined with reasonable to very good consistency. Sulfur concentrations were reported hourly for 168 h (1 week) and $SO_4^=$ concentrations every 6 h. Several of the sampling systems employed modified Meloy instruments that used FPD methods to measure sulfur with frequencies of from 3/min to every 20 min. An automated dichotomous sampler, whose fine particle stage was coupled to a wavelength X-ray fluorescence spectrometer, performed very well. Its fine particle filters were analyzed periodically (every half-hour) to obtain sulfur concentrations.

The intercomparison must be considered successful even though 4 of the 11 sulfur and $SO_4^=$ sampling systems suffered probable calibration errors. In fact, these four erroneous data sets demonstrate how easy it is to assume that monitoring instruments are properly calibrated when they really are not. Participants whose values differed from the composite means were provided with a unique opportunity to re-examine all aspects of their measurement processes and detect the causes for differences. For these reasons, more intrastate,

interstate, and federally funded intercomparison studies should be encouraged and carried out. No more valuable way is available for the scientists who make field measurements to obtain feedback information on the performance of their sampling systems. These same systems may ultimately be used to obtain pollutant concentrations for regional, state, or federal monitoring programs; hence, their concentration results need to be obtained as accurately as possible.

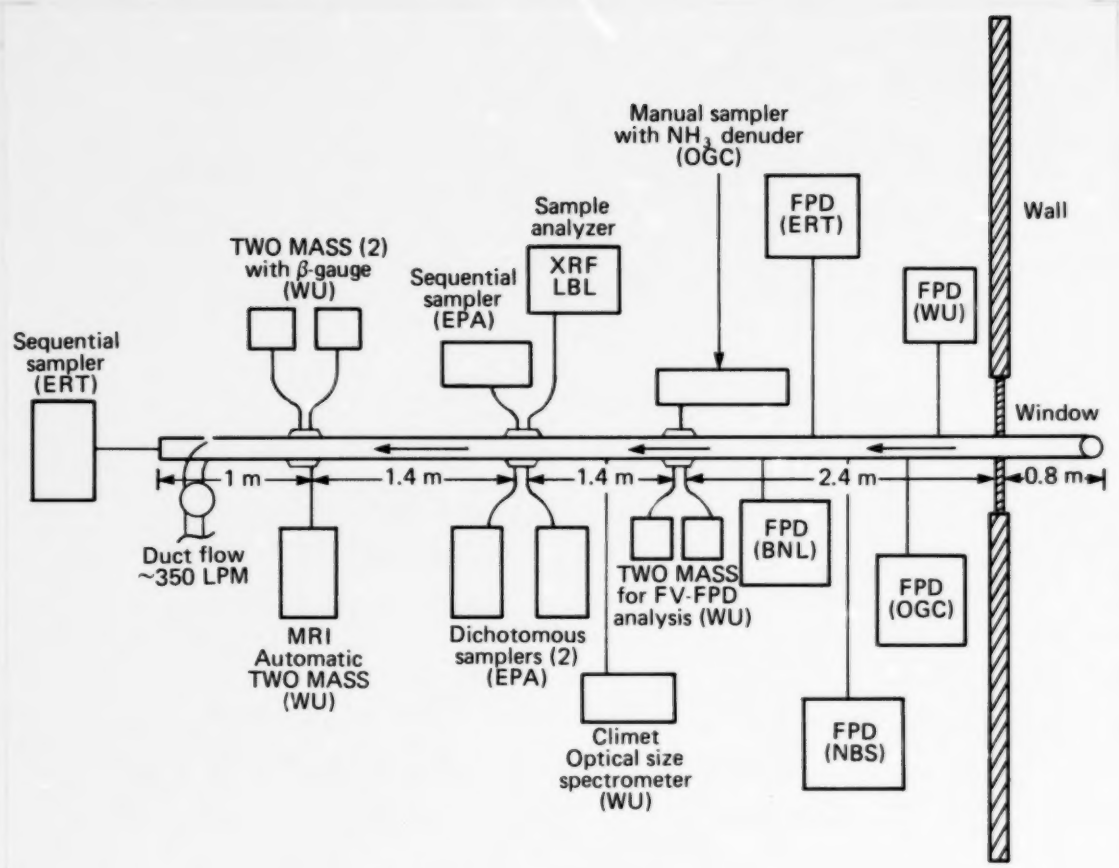

Figure 1. Top or plane view showing how each sampler was connected to the common inlet duct used for the intercomparison study. The instruments were assembled in a fourth-floor Bryan Hall lab on the WU campus, St. Louis, MO.

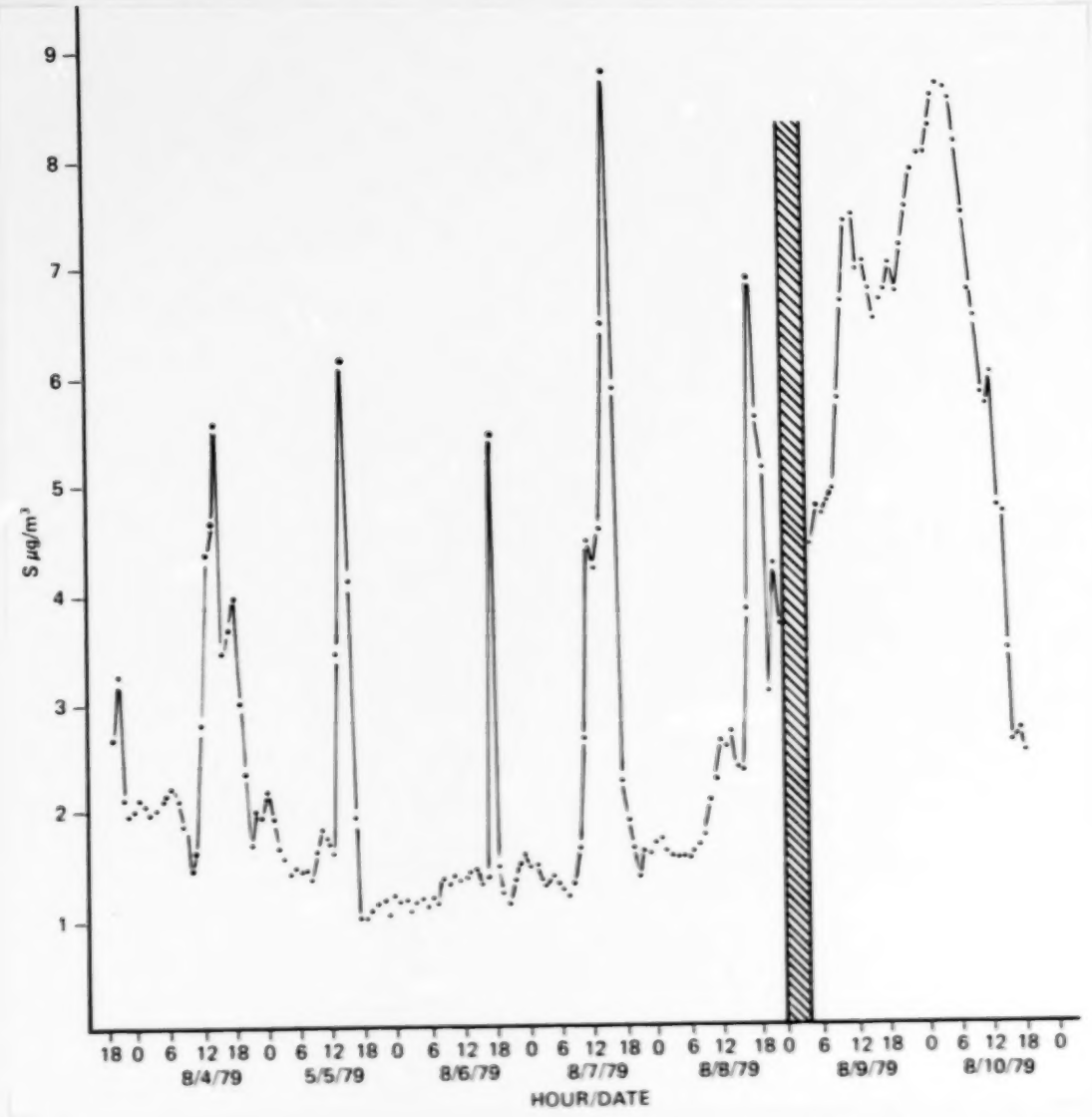

Figure 2. The calculated composite-mean sulfur concentrations, determined from six different sampling system results, are plotted as a function of time (hourly) for the week-long intercomparison study. The 5-h period beginning at 2300 CDT on 8/8/79 was a calibration period. Note that air stagnation occurred during the last 40 h. See text for a discussion of the sulfur excursions.

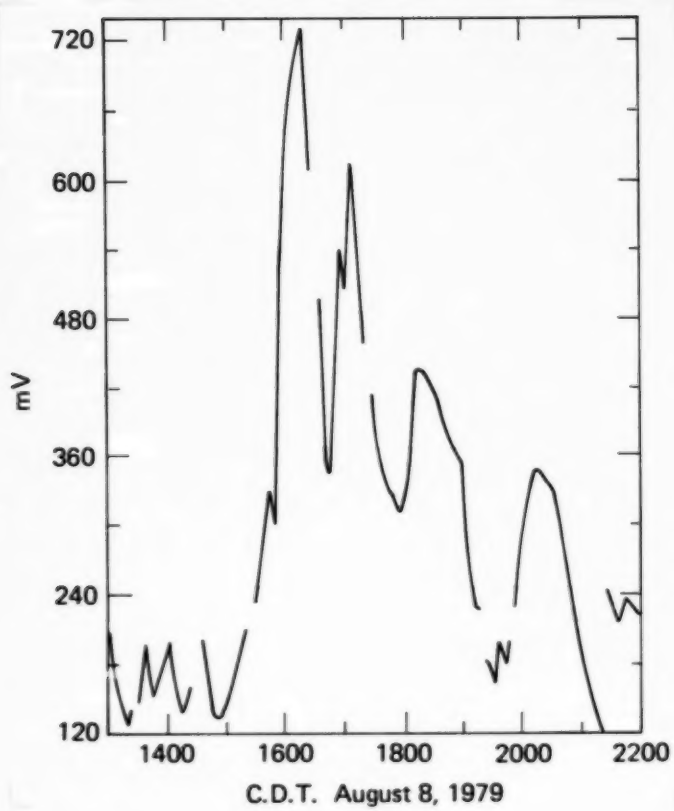

Figure 3. Relative sulfur concentration versus time recorded by the BNL sampler at three measurements per minute are shown as continuous lines. These data show the multipeaked fine structure typical of the daily transient sulfur excursions encountered.

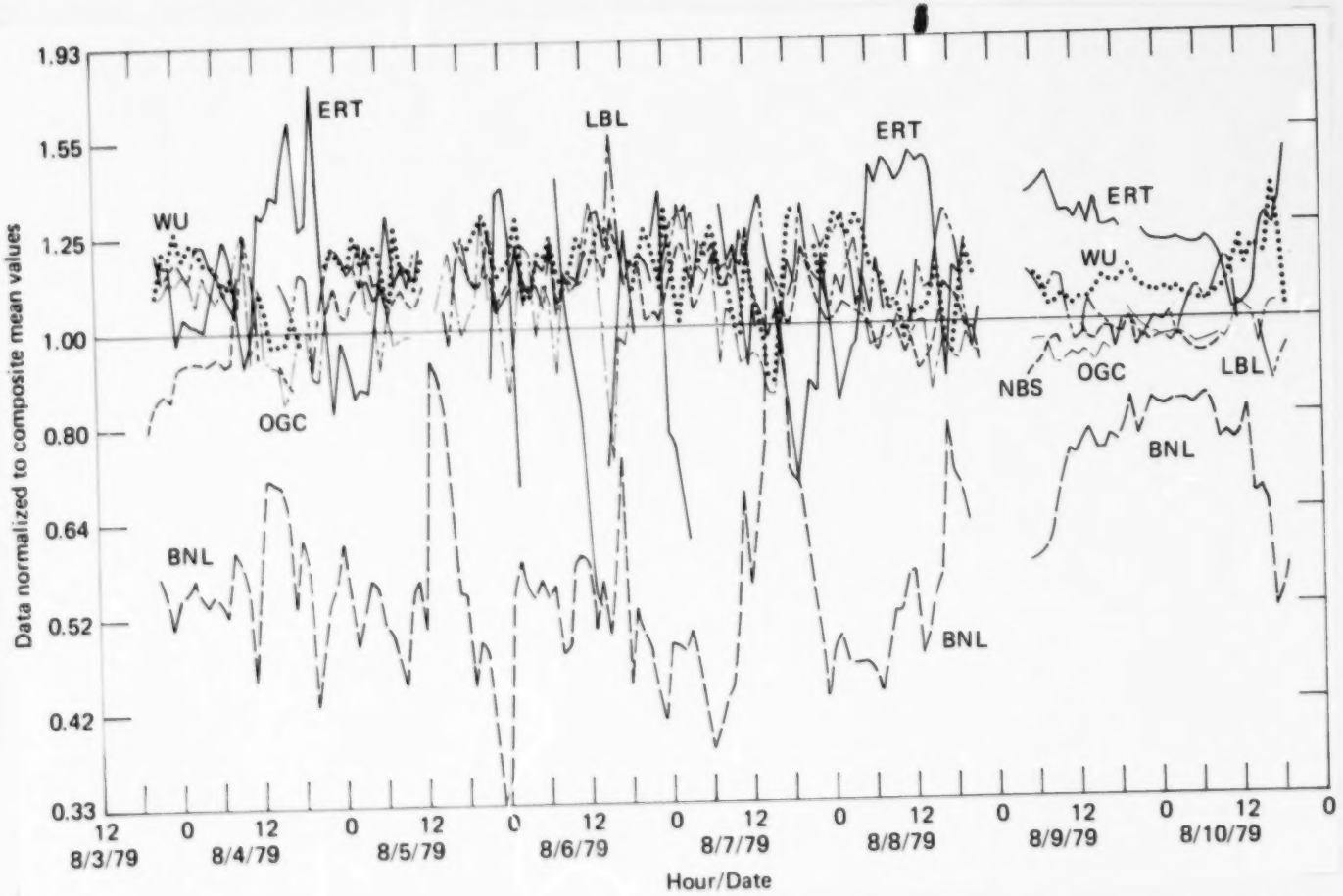

Figure 4. Reported hourly sulfur concentrations from six sampling systems plotted as a function of time for the duration of the study. All samplers observed each sulfur excursion. Calibration differences are responsible for the differing concentrations reported.

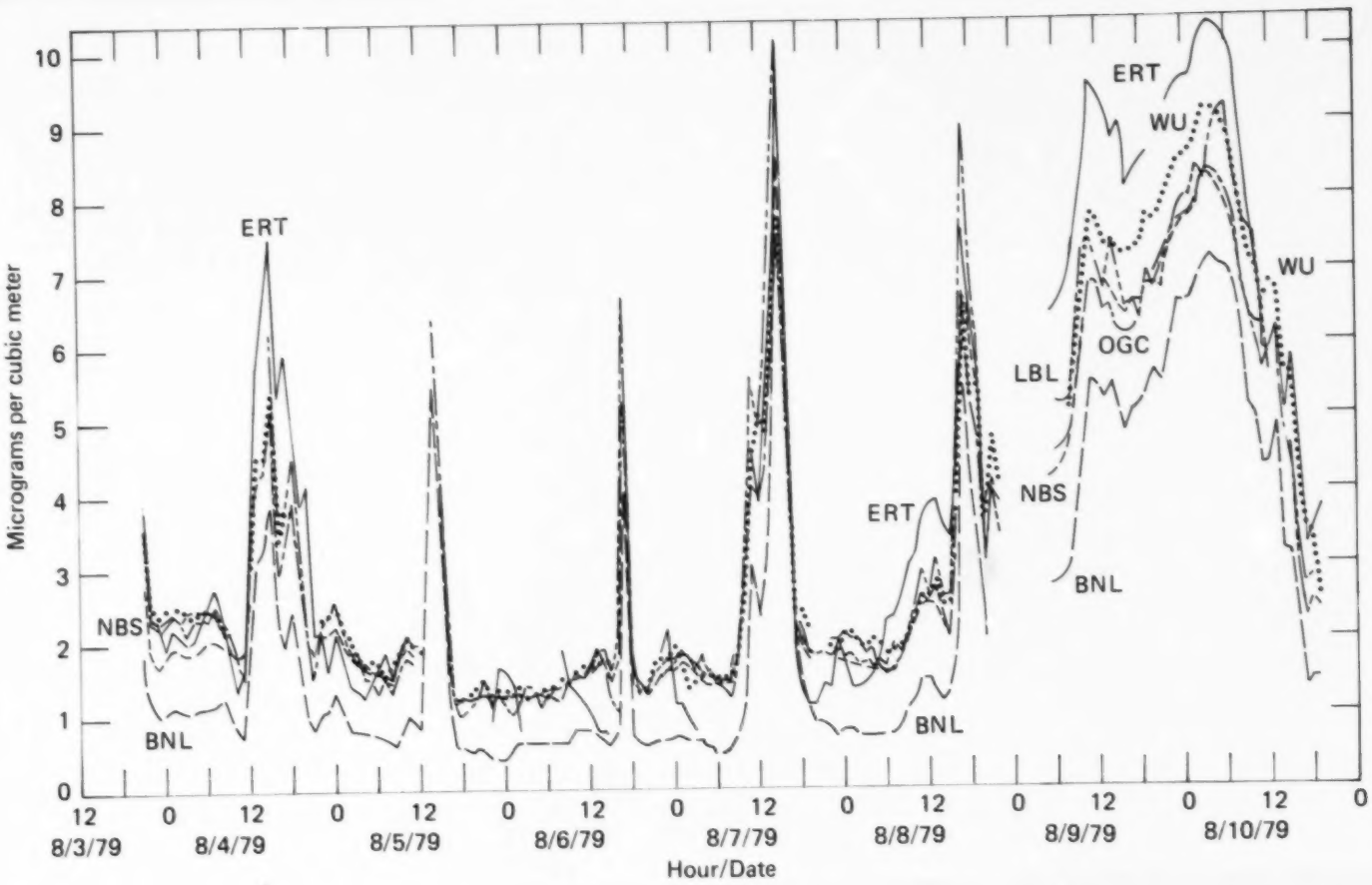

Figure 5. Hourly sulfur concentrations from six sampling systems are shown normalized to the calculated, hourly, composite mean concentration values. Percent deviation of each sampler's results can be interpreted directly from the ordinate scale. BNL values are generally low while ERT values are high.

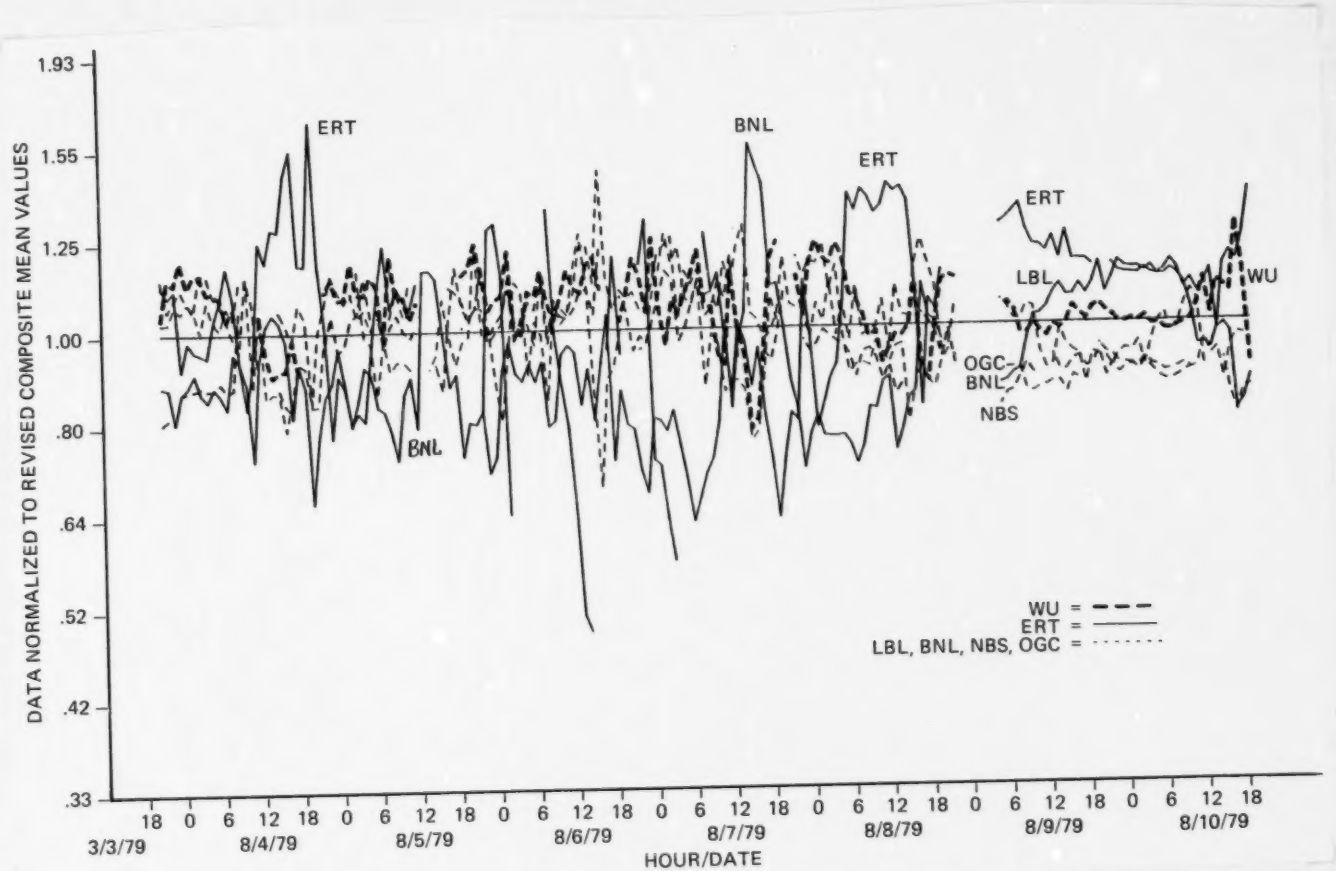

Figure 6. The same hourly sulfur concentrations for five of the six sampling systems as shown in Figure 5, plus BNL's revised data. Note that the latter's higher data cause a 6.2% absolute increase in the composite-mean concentrations relative to that shown in Figure 5.

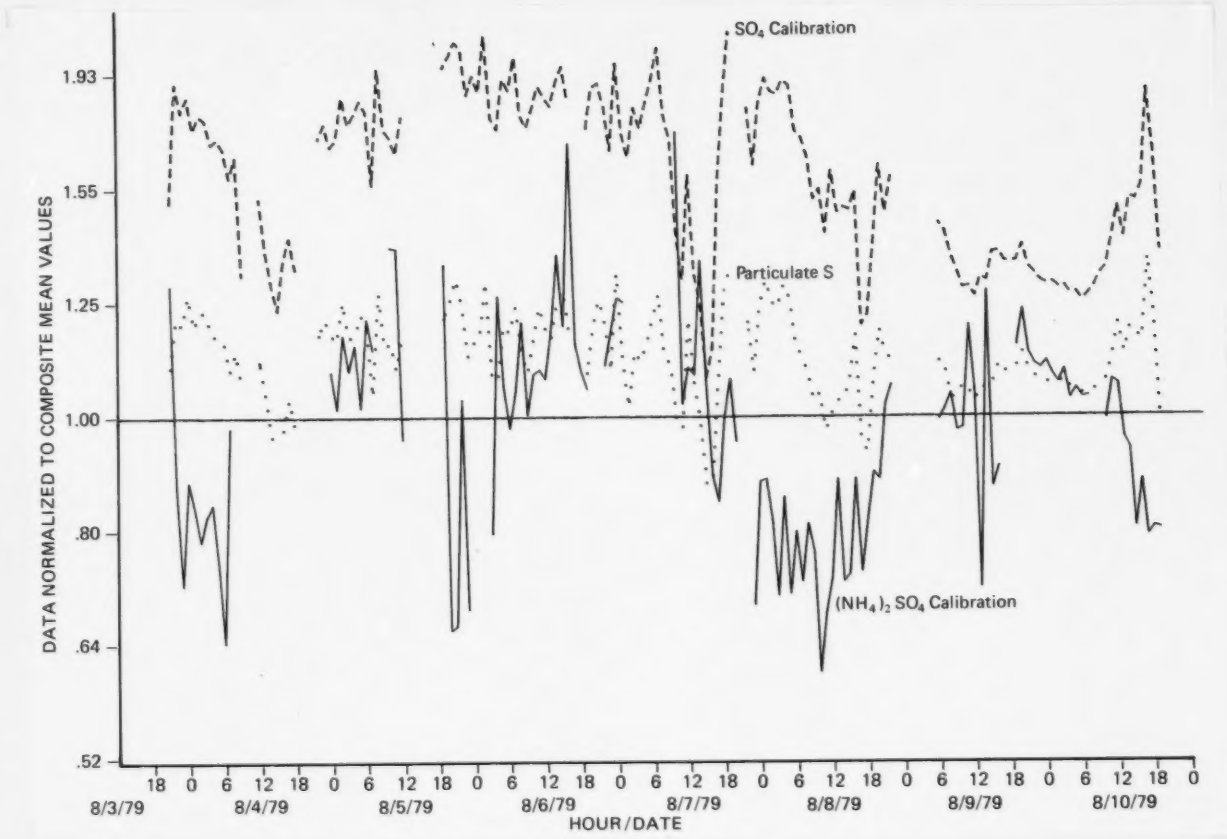

Figure 7. Hourly sulfur concentrations for three WU sampling systems, each based on the different calibration methods indicated, are shown normalized to the original composite-mean concentration values. Compare the relatively very high concentration WU SO_2-based results shown here with BNL's relatively low results shown in Figure 5.

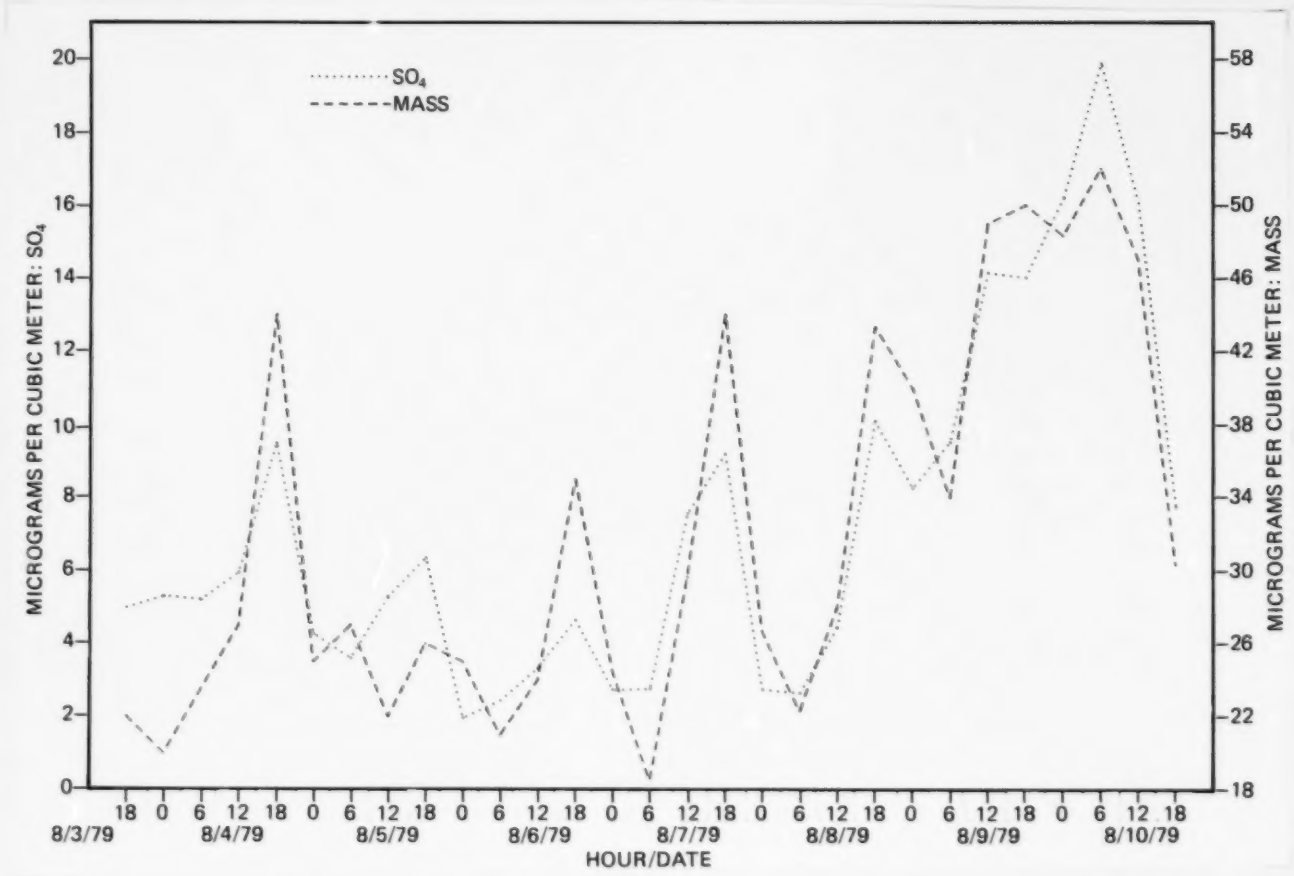

Figure 8. Composite-mean 6-h $SO_4^=$ concentrations (dotted curve--left ordinate) and composite-mean mass concentrations (dashed curve--right ordinate) are shown as a function of time for the week-long study. Note the suppressed zero of the mass scale.

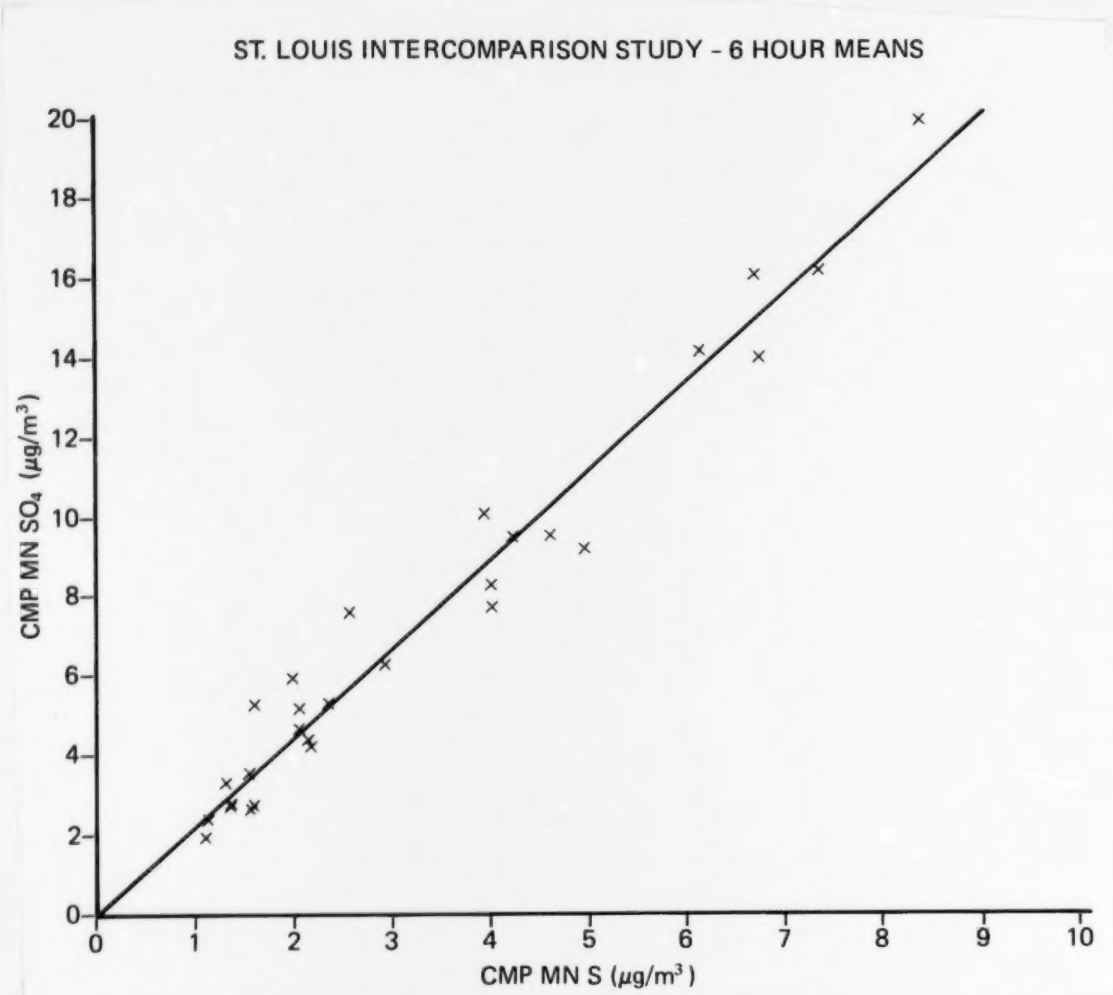

Figure 9. A regression analysis plot of 6-h composite-mean $SO_4^=$ concentrations versus 6-h composite-mean sulfur concentrations. In several recent studies (1-3) the $SO_4^=$ to sulfur ratio observed was 3.0.

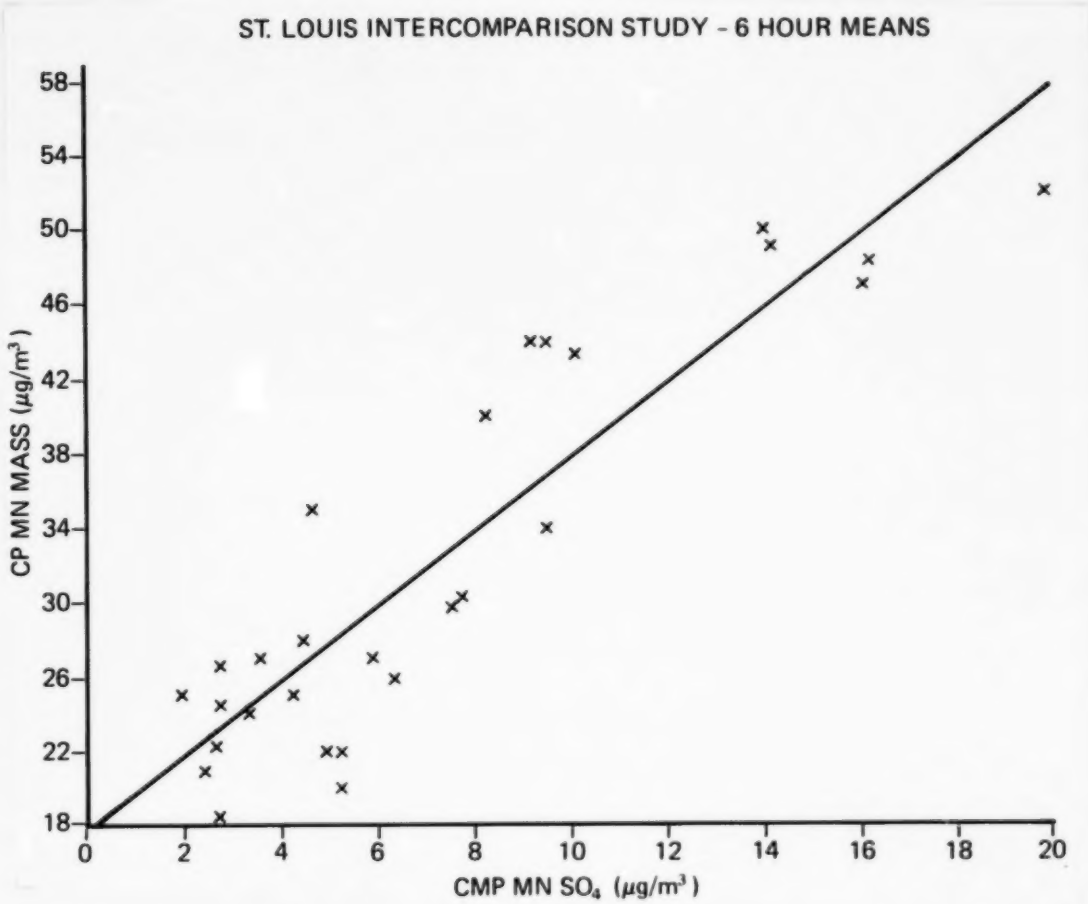

Figure 10. A regression analysis plot of 6-h composite-mean fine ($\leq$ 2.5 μm) mass concentrations versus 6-h composite-mean $SO_4^=$ concentrations. This was an unexpected correlation. Note the suppressed zero for the mass concentration scale.

TABLE 1. PARTICIPANTS IN THE ST. LOUIS INTERCOMPARISON STUDY

Sampler type	Participant	Institution	Meas. period	No. values reported	Reference
		Sulfur			
Meloy SA-285	Coburn	WU	15 min	148/163	(6)
Meloy SA-285 modified	Huntzicker	OGC	20 min	157/163	(7)
Meloy SA-285 modified	Collins	ERT	1 min	143/163	(10)
Meloy SA-260 modified	Tanner	BNL	3/min	159/163	(9)
Meloy SA-285 modified	McKenzie	NBS	1 min	140/163	(8)
Dichotomous plus wavelength XRF	Jaklevic	LBL	30 min	159/163	(11)
		$SO_4^=$			
Sequential sampler	Collins	ERT	6 h	22/29	(10)
Dichotomous automated	Stevens	EPA	6 h	24/29	(3)
Sequential hi-vol	Tanner	BNL	6 h	28/29	(9)
		Mass			
TWOMASS1	Cobourn	WU	hourly	*	(6)
TWOMASS 2	Cobourn	WU	hourly	*	(6)
Dichotomous automated	Stevens	EPA	hourly	*	(6)

*Mass data were reported on an irregular basis (see text).

TABLE 2. SIX-HOUR $SO_4^=$ AND COMPOSITE-MEAN $SO_4^=$, SULFUR, AND MASS MEANS*

Date	End Time (CDT)	$SO_4^=$ (μg/m³) ERT	BNL	EPA	Mean $SO_4^=$ CM $SO_4^=$	Mean Sulfur CM S	Mean M_f fine Mass
8/3/79	1800	-	-	4.95	4.95	-	22
	2400	-	5.17	5.36	5.26	2.38	20
8/4/79	0600	-	5.18	-	5.18	2.06	-
	1200	4.37	7.46	-	5.91	1.99	27
	1800	8.62	10.29	-	9.46	4.26	44
	2400	3.83	4.52	4.36	4.24	2.18	25
8/5/79	0600	2.90	3.75	4.07	3.57	1.57	27
	1200	-	5.61	4.92	5.26	1.60	22
	1800	-	7.25	5.38	6.31	2.94	26
	2400	1.15	2.29	2.38	1.94	1.12	25
8/6/79	0600	1.90	2.21	3.17	2.43	1.14	21
	1200	2.71	3.73	3.50	3.13	1.32	24
	1800	6.59	4.68	2.63	4.63	2.07	35
	2400	2.60	3.01	2.57	2.73	1.37	25
8/7/79	0600	2.62	3.25	2.38	2.75	1.35	18
	1200	6.70	9.21	6.73	7.55	2.58	30
	1800	7.53	9.47	10.52	9.17	4.97	44
	2400	2.27	3.18	2.77	2.74	1.60	27
8/8/79	0600	1.80	3.15	2.97	2.64	1.57	22
	1200	3.88	5.09	4.36	4.44	2.16	28
	1800	8.95	11.58	9.70	10.08	3.96	43
	2400	-	8.24	-	8.24	4.03	40
8/9/79	0600	-	9.50	-	9.50	4.63	34
	1200	13.50	14.40	14.48	14.13	6.16	49
	1800	9.47	16.25	16.29	14.00	6.77	50
	2400	12.91	18.10	17.52	16.18	7.38	48
8/10/79	0600	18.48	20.20	20.88	19.85	8.43	52
	1200	14.53	16.75	16.80	16.03	6.72	47
	1900	6.53	8.99	7.68	7.73	4.04	30

*Means computed using original BNL data.

TABLE 3. REGRESSION ANALYSIS SUMMARY FOR HOURLY SULFUR CONCENTRATIONS

Composite Mean	LAB					
	LBL	NBS	OGC	WU	BNL*	ERT
Slope	1.030	0.939	0.909	1.019	0.877	1.224
± error	0.021	0.015	0.013	0.016	0.022	0.035
Intercept	0.170	0.181	0.269	0.240	-0.635	-0.174
± error	0.084	0.058	0.051	0.063	0.089	0.143
R	0.988	0.993	0.994	0.993	0.982	0.979
E ($\mu g/m^3$)	0.374	0.250	0.221	0.272	0.392	0.591

Composite Mean	LAB					
	LBL	NBS	OGC	WU	BNL†	ERT
Slope	0.961	0.883	0.848	0.952	1.195	1.142
± error	0.020	0.014	0.012	0.016	0.026	0.034
Intercept	0.175	0.179	0.274	0.251	-0.678	-0.161
± error	0.084	0.058	0.050	0.067	0.113	0.149
R	0.988	0.994	0.995	0.993	0.986	0.978
E ($\mu g/m^3$)	0.373	0.248	0.221	0.291	0.502	0.615

*BNL original data.

†BNL revised data.

TABLE 4. REGRESSION ANALYSES SUMMARY FOR 6-H $SO_4^=$ AND MASS RESULTS

Composite Mean	6-h $SO_4^=$			6-h $SO_4^=$ vs. 6-h Sulfur Using:	
	EPA	BNL	ERT	Original BNL	Revised BNL
Slope	1.080	1.054	0.851	2.22	2.13
± error	0.053	0.041	0.097	0.14	0.14
Intercept	-0.390	0.218	0.313	0.00	-0.07
± error	0.464	0.357	0.876	0.56	0.58
R	0.99	0.99	0.96	0.98	0.98
E ($\mu g/m^3$)	0.77	0.60	1.4	0.94	0.96

Composite Mean	6-h Mass			Mf vs. $SO_4^=$
	WU1	WU2	EPA	
Slope	1.035	0.827	1.082	2.00
± error	0.150	0.108	0.135	0.31
Intercept	-0.466	7.26	-4.99	17.71
± error	5.98	3.75	4.16	2.75
R	0.96	0.94	0.94	0.91
E ($\mu g/m^3$)	3.0	3.3	3.5	4.6

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Lawrence Berkeley Laboratory

HOURLY SULFUR CONCENTRATIONS ($\mu g/m^3$)

END TIME	8/3/79	8/4/79	8/5/79	8/6/79	8/7/79	8/8/79	8/9/79	8/10/79
0100	--	2.41	2.20	1.26	1.89	1.82	--	7.94
0200	--	2.28	1.92	1.31	1.75	1.66	--	8.37
0300	--	2.42	1.70	1.21	1.70	1.83	--	8.17
0400	--	2.46	1.60	1.31	1.51	1.61	4.40	8.81
0500	--	2.45	1.55	1.24	1.60	1.73	5.32	9.12
0600	--	2.45	1.57	1.23	1.47	1.62	5.20	9.18
0700	--	2.43	1.57	1.36	1.44	1.93	5.15	8.44
0800	--	2.20	1.48	1.37	1.49	1.81	5.26	7.86
0900	--	1.87	1.89	1.47	1.88	2.18	6.39	7.49
1000	--	1.80	2.01	1.56	2.93	2.38	7.33	7.49
1100	--	1.84	2.09	1.50	5.57	2.94	7.39	6.55
1200	--	2.62	--	1.61	4.89	2.58	7.08	5.54
1300	--	--	--	1.84	5.90	3.12	6.67	--
1400	--	5.20	6.50	1.88	8.74	2.57	7.37	5.16
1500	--	6.21	4.39	1.56	10.14	2.56	6.83	4.61
1600	--	3.74	1.85	2.12	6.49	4.67	6.47	3.14
1700	--	3.78	1.15	6.69	2.39	8.98	6.58	2.24
1800	--	4.49	1.26	1.61	2.02	6.89	6.29	2.47
1900	--	3.37	1.20	1.43	1.83	5.99	6.95	2.35
2000	2.86	2.12	1.24	1.32	1.81	3.09	6.71	--
2100	3.89	1.79	1.29	1.56	1.83	4.02	7.03	--
2200	2.37	2.26	1.17	1.65	1.77	3.84	7.19	--
2300	2.24	2.35	1.25	1.76	1.84	--	7.78	--
2400	2.33	2.59	1.23	1.74	1.75	--	7.97	--

National Bureau of Standards

HOURLY SULFUR CONCENTRATIONS ($\mu g/m^3$)

END TIME	8/3/79	8/4/79	8/5/79	8/6/79	8/7/79	8/8/79	8/9/79	8/10/79
0100	--	1.95	1.99	1.29	1.71	1.66	--	7.70
0200	--	1.90	1.81	1.28	1.65	1.63	--	7.82
0300	--	1.85	1.72	1.27	1.54	1.61	--	8.25
0400	--	1.87	1.73	1.27	1.44	1.59	3.93	8.23
0500	--	1.96	1.60	1.31	1.40	1.57	4.17	8.02
0600	--	2.03	1.60	1.34	1.41	1.57	4.25	7.85
0700	--	2.05	1.48	1.39	1.41	1.56	4.37	7.53
0800	--	1.95	1.45	1.41	1.42	1.75	4.61	6.97
0900	--	2.09	1.79	1.48	1.81	2.09	5.57	6.39
1000	--	--	1.94	1.53	3.13	2.22	6.27	6.22
1100	--	--	1.83	1.49	5.12	2.44	--	--
1200	--	2.53	1.78	1.55	5.28	2.50	8.26	--
1300	--	--	--	1.66	4.53	2.42	6.82	--
1400	--	4.28	--	1.69	6.37	2.19	6.69	--
1500	--	5.16	--	1.45	--	--	6.45	--
1600	--	3.08	2.27	1.76	6.18	3.70	6.35	--
1700	--	3.20	1.24	--	2.33	7.54	6.57	--
1800	--	--	1.19	1.70	1.89	6.00	6.55	--
1900	--	--	1.21	1.41	1.75	5.37	6.79	--
2000	2.10	--	1.25	1.28	1.67	3.03	6.80	--
2100	2.77	1.95	1.29	1.36	--	4.21	6.72	--
2200	1.84	2.05	1.29	1.55	1.73	3.35	7.26	--
2300	1.67	2.14	1.27	1.61	1.72	--	7.43	--
2400	1.82	2.25	1.26	1.60	1.70	--	7.65	--

Oregon Graduate Center

HOURLY SULFUR CONCENTRATIONS ($\mu g/m^3$)

END TIME	8/3/79	8/4/79	8/5/79	8/6/79	8/7/79	8/8/79	8/9/79	8/10/79
0100	--	2.40	2.30	1.00	1.80	2.00	--	7.70
0200	--	2.30	1.90	1.10	1.80	2.00	--	7.90
0300	--	2.10	1.90	1.40	1.60	1.80	--	8.30
0400	--	2.30	1.50	1.40	1.80	1.90	--	8.30
0500	--	2.30	1.50	1.10	1.50	1.60	4.50	8.20
0600	--	2.30	1.30	1.30	1.40	1.50	4.50	8.00
0700	--	2.50	1.50	1.20	1.40	1.60	4.60	7.70
0800	--	2.30	1.30	1.20	1.20	1.70	4.70	7.10
0900	--	2.20	1.60	1.50	1.70	2.00	5.20	6.50
1000	--	1.80	1.80	1.50	2.70	2.30	6.00	6.20
1100	--	1.50	1.70	1.50	4.10	2.60	6.80	5.60
1200	--	3.10	--	1.70	3.90	2.50	6.80	5.90
1300	--	4.10	3.70	1.90	4.30	2.70	6.40	6.10
1400	--	4.30	6.40	1.70	5.90	2.40	6.50	4.80
1500	--	5.10	4.50	1.20	7.50	2.00	6.10	4.40
1600	--	2.90	2.30	1.00	5.00	3.50	6.10	3.50
1700	--	3.30	1.10	5.30	2.20	6.70	6.20	2.70
1800	--	3.90	1.00	1.40	2.20	5.20	--	2.80
1900	--	3.00	1.10	1.30	1.80	4.70	6.60	--
2000	2.90	2.10	1.20	--	--	3.00	6.90	--
2100	3.50	1.50	1.50	1.40	2.10	4.00	7.10	--
2200	2.30	2.10	1.10	1.50	2.00	3.40	7.40	--
2300	2.20	2.10	1.30	1.60	2.00	--	7.60	--
2400	2.20	--	1.10	1.70	2.10	--	7.70	--

Environmental Research and Technology

HOURLY SULFUR CONCENTRATIONS ($\mu g/m^3$)

END TIME	8/3/79	8/4/79	8/5/79	8/6/79	8/7/79	8/8/79	8/9/79	8/10/79
0100	--	2.19	1.80	1.42	1.14	1.36	--	9.57
0200	--	2.08	1.41	.75	.92	1.37	--	9.84
0300	--	2.00	1.36	--	.79	1.46	--	10.27
0400	--	2.02	1.23	--	--	1.51	6.69	10.32
0500	--	2.30	1.46	--	--	1.74	6.40	10.20
0600	--	2.47	1.67	--	--	2.30	6.43	10.09
0700	--	2.75	1.88	.82	.93	2.31	6.67	9.78
0800	--	2.42	1.51	1.89	1.73	2.57	6.94	8.89
0900	--	1.81	1.91	1.38	1.89	2.99	7.64	7.87
1000	--	1.32	2.09	1.30	3.20	3.13	8.52	7.20
1100	--	1.60	1.96	1.15	4.64	3.69	9.53	5.91
1200	--	3.68	1.97	.97	3.83	3.84	9.36	5.85
1300	--	5.68	--	.77	4.91	3.91	9.03	6.21
1400	--	6.36	--	.75	6.64	3.49	8.72	5.05
1500	--	7.53	--	--	8.55	3.38	8.96	5.79
1600	--	5.33	--	.91	6.09	4.46	8.05	4.38
1700	--	5.96	--	5.70	2.00	6.07	8.27	3.22
1800	--	4.94	.81	1.83	1.50	6.34	8.46	3.56
1900	--	3.83	1.14	1.23	1.13	5.67	8.55	3.76
2000	3.83	4.14	--	--	1.13	3.73	--	--
2100	3.83	2.10	.77	1.45	1.42	--	8.94	--
2200	2.45	2.14	.92	1.84	1.36	--	9.21	--
2300	2.29	1.60	1.64	2.16	1.98	--	9.46	--
2400	1.92	2.12	1.60	1.15	1.75	--	9.56	--

Brookhaven National Laboratory

HOURLY SULFUR CONCENTRATIONS ($\mu g/m^3$)

END TIME	8/3/79	8/4/79	8/5/79	8/6/79	8/7/79	8/8/79	8/9/79	8/10/79
0100	--	1.15	1.07	.63	.71	.80	--	6.55
0200	--	1.15	.80	.63	.64	.71	--	6.84
0300	--	1.07	.80	.63	.64	.71	--	7.04
0400	--	1.07	.80	.63	.64	.71	2.62	7.18
0500	--	1.15	.80	.63	.55	.71	2.73	7.04
0600	--	1.15	.72	.63	.47	.71	2.73	7.04
0700	--	1.15	.72	.63	.47	.71	2.83	6.84
0800	--	1.26	.63	.63	.55	.81	2.93	6.11
0900	--	1.07	.72	.63	.71	1.07	3.77	5.10
1000	--	.80	.98	.80	1.33	1.16	4.69	5.01
1100	--	.72	.98	.80	3.05	1.46	5.48	4.36
1200	--	1.68	.80	.80	2.30	1.46	5.46	4.36
1300	--	3.11	3.21	.71	2.94	1.26	5.25	4.89
1400	--	3.26	5.51	.80	4.71	1.16	5.46	3.17
1500	--	3.90	3.42	.64	10.00	1.26	5.01	3.17
1600	--	2.25	1.26	.77	6.34	2.14	4.82	2.25
1700	--	1.93	.55	4.04	2.12	5.46	5.10	1.33
1800	--	2.42	.55	.64	1.33	3.94	5.10	1.44
1900	--	1.73	.47	.64	1.15	3.50	5.46	1.44
2000	1.44	.98	.55	.55	.89	1.94	5.63	--
2100	1.84	.80	.55	.64	.89	--	5.46	--
2200	1.15	1.07	.40	.64	.80	--	5.97	--
2300	.98	1.07	.40	.64	.71	--	6.55	--
2400	1.07	1.33	.40	.71	.80	--	6.55	--

Brookhaven National Laboratory - Revised

0100	--	1.97	1.82	1.13	1.27	1.40	--	9.70
0200	--	1.97	1.40	1.13	1.13	1.27	--	10.00
0300	--	1.82	1.40	1.13	1.13	1.27	--	10.20
0400	--	1.82	1.40	1.13	1.13	1.27	4.22	10.50
0500	--	1.97	1.40	1.13	.98	1.27	4.38	10.20
0600	--	1.97	1.27	1.13	.84	1.27	4.38	10.20
0700	--	1.97	1.27	1.13	.84	1.27	4.55	10.00
0800	--	2.12	1.13	1.13	.98	1.40	4.69	9.00
0900	--	1.82	1.27	1.13	1.27	1.82	5.91	7.80
1000	--	1.40	1.67	1.40	2.26	1.97	7.20	7.70
1100	--	1.27	1.67	1.40	4.85	2.43	8.10	6.70
1200	--	2.79	1.40	1.40	3.68	2.43	8.20	6.70
1300	--	4.89	5.06	1.27	4.72	2.12	7.90	7.50
1400	--	5.19	8.10	1.40	7.10	1.97	8.20	5.02
1500	--	6.06	5.39	1.13	15.20	2.12	7.70	5.02
1600	--	3.59	2.12	1.34	9.40	3.47	7.40	3.61
1700	--	3.16	.98	6.19	3.46	8.10	7.80	2.26
1800	--	3.89	.98	1.13	2.26	6.07	7.80	2.41
1900	--	2.86	.84	1.13	1.97	5.51	8.20	2.41
2000	2.43	1.67	.98	.98	1.53	3.16	8.40	--
2100	3.02	1.40	.98	1.13	1.53	--	8.20	--
2200	1.97	1.82	.92	1.13	1.40	--	8.90	--
2300	1.67	1.82	.92	1.13	1.27	--	9.70	--
2400	1.82	2.26	.92	1.27	1.40	--	9.70	--

Washington University - Ammonium Sulfate

HOURLY SULFUR CONCENTRATIONS ($\mu g/m^3$)

END TIME	8/3/79	8/4/79	8/5/79	8/6/79	8/7/79	8/8/79	8/9/79	8/10/79
0100	--	2.49	2.23	1.35	1.65	2.11	--	8.57
0200	--	2.49	2.06	1.40	1.38	1.93	--	8.79
0300	--	2.41	1.80	1.24	1.46	1.91	--	9.16
0400	--	2.35	1.66	1.26	1.54	2.00	--	9.13
0500	--	2.46	1.76	1.34	1.51	1.94	5.43	9.07
0600	--	2.48	1.69	1.38	1.51	1.81	5.25	8.85
0700	--	2.42	1.50	1.40	1.51	1.87	5.28	8.45
0800	--	2.36	1.71	1.51	1.46	1.91	5.10	7.84
0900	--	1.94	1.86	1.43	1.81	2.14	5.96	7.16
1000	--	--	2.10	1.60	2.63	2.36	7.06	6.99
1100	--	2.39	1.91	1.67	4.37	2.54	7.76	6.50
1200	--	3.09	1.88	1.63	5.08	2.59	7.64	6.80
1300	--	4.55	--	1.65	4.85	2.78	7.31	6.74
1400	--	4.47	--	1.79	6.39	2.45	7.38	5.65
1500	--	5.39	--	1.66	7.71	2.51	7.20	5.49
1600	--	3.35	--	1.60	5.16	4.47	7.19	3.98
1700	--	3.79	--	--	2.40	6.58	7.26	3.53
1800	--	3.80	1.27	1.57	2.41	5.22	7.33	3.29
1900	--	--	1.29	1.33	2.17	5.50	7.72	2.49
2000	2.76	--	1.41	1.33	--	3.63	7.61	--
2100	3.55	1.98	1.50	1.69	1.81	4.78	7.83	--
2200	2.55	2.33	1.27	1.79	1.91	4.10	8.12	--
2300	2.32	2.33	1.35	1.73	1.83	--	8.39	--
2400	2.49	2.54	1.33	1.94	2.10	--	8.50	--

Washington University - Particulate Sulfur

HOURLY SULFUR CONCENTRATIONS ($\mu g/m^3$)

END TIME	8/3/79	8/4/79	8/5/79	8/6/79	8/7/79	8/8/79	8/9/79	8/10/79
0100	--	1.76	1.96	--	1.85	1.44	--	8.67
0200	--	1.60	1.93	.77	--	1.27	--	8.80
0300	--	1.63	1.69	.92	--	1.10	--	9.32
0400	--	1.70	1.63	1.48	--	1.33	--	8.95
0500	--	1.58	1.47	1.19	--	1.10	4.70	9.07
0600	--	1.39	1.72	1.15	--	1.27	4.70	8.80
0700	--	2.17	1.64	1.19	--	1.21	4.89	8.43
0800	--	--	--	1.60	--	1.43	5.14	--
0900	--	--	1.70	1.32	1.67	1.60	5.60	6.37
1000	--	--	2.52	1.50	4.58	1.38	6.50	6.48
1100	--	--	2.41	1.48	4.58	1.79	8.80	6.19
1200	--	--	1.54	1.48	4.63	1.89	7.78	6.04
1300	--	--	--	1.68	4.95	2.39	4.97	5.74
1400	--	--	--	1.96	8.71	1.73	8.93	4.47
1500	--	--	--	1.55	9.38	1.73	5.90	3.79
1600	--	--	--	2.30	5.24	3.39	5.90	3.05
1700	--	--	--	6.25	1.90	5.11	--	2.07
1800	--	--	1.68	1.59	1.88	4.59	6.49	2.19
1900	--	--	1.43	1.29	1.76	4.60	8.03	2.02
2000	2.43	--	.75	--	1.31	2.72	8.26	--
2100	4.15	--	.77	1.79	--	4.35	8.11	--
2200	1.83	--	1.06	1.65	.88	3.90	8.31	--
2300	1.41	2.09	.83	1.86	1.17	--	8.62	--
2400	1.74	2.36	--	1.85	1.50	--	8.87	--

Washington University - Sulfur Dioxide

HOURLY SULFUR CONCENTRATIONS ($\mu g/m^3$)

END TIME	8/3/79	8/4/79	8/5/79	8/6/79	8/7/79	8/8/79	8/9/79	8/10/79
0100	--	3.64	3.29	2.16	2.55	3.11	--	10.34
0200	--	3.63	3.05	2.24	2.23	2.89	--	10.56
0300	--	3.49	2.71	2.04	2.33	2.88	--	10.95
0400	--	3.40	2.54	2.04	2.41	2.96	--	10.93
0500	--	3.59	2.65	2.15	2.40	2.92	6.97	10.90
0600	--	3.59	2.56	2.20	2.39	2.74	6.84	10.60
0700	--	3.51	2.25	2.26	2.42	2.84	6.86	10.25
0800	--	3.43	2.63	2.38	2.33	2.89	6.70	9.56
0900	--	2.40	2.83	2.29	2.78	3.15	7.60	8.85
1000	--	--	3.11	2.50	3.76	3.49	8.50	8.66
1100	--	3.04	2.89	2.55	5.81	3.71	9.48	8.14
1200	--	4.23	2.86	2.54	6.70	4.13	9.35	8.50
1300	--	6.01	--	2.58	6.01	3.99	9.03	8.43
1400	--	5.99	--	2.73	8.01	3.55	9.10	7.24
1500	--	6.81	--	2.55	9.46	3.48	9.25	7.09
1600	--	4.64	--	2.48	6.69	5.89	8.91	5.36
1700	--	5.16	--	--	3.50	8.20	8.96	4.86
1800	--	5.19	2.08	2.43	3.49	6.80	9.06	4.51
1900	--	--	2.09	2.13	3.42	7.10	9.44	3.44
2000	4.00	--	2.26	2.11	--	4.97	9.34	--
2100	4.88	2.95	2.36	2.56	2.74	6.28	9.56	--
2200	4.00	3.40	2.08	2.71	2.88	5.81	9.88	--
2300	3.50	3.39	2.23	2.64	2.72	--	10.19	--
2400	3.64	3.64	2.22	2.90	3.10	--	10.28	--

Composite Mean

HOURLY SULFUR CONCENTRATIONS ($\mu g/m^3$)

END TIME	8/3/79	8/4/79	8/5/79	8/6/79	8/7/79	8/8/79	8/9/79	8/10/79
0100	--	2.10	1.93	1.16	1.48	1.63	--	8.01
0200	--	2.03	1.65	1.08	1.36	1.55	--	8.26
0300	--	1.98	1.55	1.15	1.29	1.55	--	8.53
0400	--	2.01	1.42	1.17	1.39	1.55	4.41	8.66
0500	--	2.10	1.45	1.12	1.31	1.55	4.76	8.61
0600	--	2.15	1.43	1.18	1.25	1.59	4.73	8.50
0700	--	2.22	1.44	1.13	1.19	1.66	4.82	8.12
0800	--	2.08	1.35	1.34	1.31	1.76	4.92	7.46
0900	--	1.83	1.63	1.32	1.63	2.08	5.76	6.75
1000	--	1.43	1.82	1.38	2.65	2.26	6.65	6.52
1100	--	1.61	1.75	1.35	4.48	2.61	7.39	5.78
1200	--	2.78	1.61	1.38	4.21	2.58	7.43	5.69
1300	--	4.36	3.46	1.42	4.57	2.70	6.91	5.99
1400	--	4.65	6.14	1.44	6.46	2.38	7.02	4.77
1500	--	5.55	4.10	1.30	8.78	2.34	6.76	4.69
1600	--	3.44	1.92	1.36	5.88	3.82	6.50	3.45
1700	--	3.66	1.01	5.43	2.24	6.89	6.66	2.60
1800	--	3.91	1.01	1.46	1.89	5.60	6.75	2.71
1900	--	2.98	1.07	1.22	1.64	5.12	7.01	2.51
2000	2.65	2.34	1.13	1.12	1.38	3.07	6.73	--
2100	3.23	1.69	1.15	1.35	1.61	4.25	7.18	--
2200	2.11	1.99	1.03	1.50	1.60	3.67	7.53	--
2300	1.95	1.93	1.20	1.58	1.68	--	7.87	--
2400	1.97	2.17	1.15	1.47	1.70	--	7.99	--

Composite Mean - Revised

0100	--	2.24	2.06	1.24	1.58	1.73	--	8.53
0200	--	2.17	1.75	1.16	1.44	1.64	--	8.79
0300	--	2.10	1.65	1.25	1.37	1.65	--	9.06
0400	--	2.14	1.52	1.27	1.48	1.65	4.81	9.22
0500	--	2.24	1.55	1.22	1.40	1.64	5.03	9.14
0600	--	2.28	1.52	1.28	1.33	1.68	5.00	9.03
0700	--	2.35	1.53	1.22	1.26	1.76	5.10	8.65
0800	--	2.23	1.43	1.42	1.38	1.86	5.22	7.94
0900	--	1.96	1.72	1.40	1.73	2.20	6.11	7.20
1000	--	1.58	1.94	1.48	2.81	2.39	7.06	6.97
1100	--	1.72	1.86	1.45	4.78	2.77	7.92	6.25
1200	--	2.97	1.76	1.48	4.44	2.74	7.89	6.16
1300	--	4.81	4.38	1.52	4.87	2.84	7.36	6.64
1400	--	4.97	7.00	1.54	6.86	2.51	7.48	5.14
1500	--	5.91	4.76	1.40	9.82	2.51	7.21	5.06
1600	--	3.67	2.14	1.46	6.39	4.05	6.93	3.72
1700	--	3.87	1.12	5.97	2.46	7.33	7.11	2.79
1800	--	4.20	1.09	1.54	2.05	5.95	7.29	2.91
1900	--	3.27	1.13	1.31	1.78	5.46	7.47	2.75
2000	2.81	2.51	1.22	1.23	1.54	3.27	7.28	--
2100	3.43	1.79	1.22	1.43	1.74	4.25	7.64	--
2200	2.25	2.12	1.11	1.58	1.70	3.67	8.01	--
2300	2.07	2.06	1.29	1.67	1.77	--	8.39	--
2400	2.10	2.35	1.24	1.57	1.80	--	8.51	--